[received by the International Bureau on 20 June 2005 (20.06.2005); original claims 1-95 are replaced by amended claims 1-50 (10 pages)]

What is claimed is:

1. A compound having the general structure:

(I),

wherein A^1 is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings

R^1, R^2, and R^3 are divalent fluorinated groups;

m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups;

q is 0 or 1;

Y^1 is –OH, $-NH-SO_2-R^4$ wherein R^4 is a monovalent fluorinated group, –NH–, $-NH-SO_2-R^5-SO_2-NH-$, or $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$, wherein A^2 is a divalent heterocyclic group and R^5, R^6, and R^7 are divalent fluorinated groups; and

Y^2 and Y^3 are –OH or $-NH-SO_2-R^4$; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y^1 is selected from the group consisting of –NH–, $-NH-SO_2-R^5-SO_2-NH-$, and $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$.

2. The compound of claim 1 wherein the compound is a small molecule.

3. The compound of claim 1 wherein the compound is a repeat unit for a polymer.

4. The compound of claim 1, 2 or 3 wherein A^1 selected from the group consisting of oxadiazole, triazole, thiadiazole, pyrazole, triazine, tetrazole, oxazole, thiazole, imidazole, benzoxazole, benzothiazole, benzimidazole, benzobisoxazole, benzobisthiazole, benzobisimidazole, bibenzoxazole, bibenzothiazole, and bibenzimidazole.

5. The compound of claim 4 wherein A^1 is selected from the group consisting of [1,3,4]oxadiazole, [1,3,4]thiadiazole, and [1,2,4]triazole.

6. The compound of claim 5 wherein A^1 is [1,3,4]oxadiazole.

7. The compound of claim 1, 2, or 3 wherein R^1, R^2, and R^3 are linear, branched, or cyclic perfluorinated or partially fluorinated saturated or unsaturated groups having 1 to 20 carbon atoms optionally containing ethereal oxygen, chlorine, bromine, or iodine atoms.

8. The compound of claim 7 wherein R^1, R^2, and R^3 are linear or branched perfluorinated saturated or unsaturated groups having 1 to 10 carbon atoms optionally containing ethereal oxygen atoms.

9. The compound of claim 8 wherein R^1, R^2, and R^3 are linear perfluorinated saturated groups having 1 to 6 carbon atoms.

10. The compound of claim 1, 2, or 3 wherein m + n + p is equal to 2 or 3.

11. The compound of claim 10 wherein m + n + p is equal to 2.

12. The compound of claim 1 or 3 wherein A^2 is a divalent aromatic heterocyclic group, such as an oxadiazole, triazole, thiadiazole, benzobisoxazole, benzobisthiazole, benzobisimidazole, bibenzoxazole, bibenzothiazole, and bibenzimidazole.

13. The compound of claim 12 wherein A^2 is [1,3,4]oxadiazole.

14. The compound of claim 1 or 3 wherein R^5, R^6, and R^7 are linear, branched, or cyclic perfluorinated or partially fluorinated saturated or unsaturated groups having 1 to 20 carbon atoms optionally containing ethereal oxygen, chlorine, bromine, or iodine atoms.

15. The compound of claim 1 or 2 wherein Y^1, Y^2, and Y^3 are each equal to –OH or $-NH-SO_2-R^4$, wherein R^4 is any monovalent fluorinated group, and q is 1.

16. The compound of claim 15 wherein R^4 is a linear, branched, or cyclic perfluorinated or partially fluorinated saturated or unsaturated group having 1 to 20 carbon atoms optionally containing ethereal oxygen, chlorine, bromine, or iodine atoms.

17. The compound of claim 15 wherein m + n + p is equal to 2 or 3.

18. The compound of claim 1 or 2 wherein Y^1 is $-NH-SO_2-R^4$, n and p are each equal to 0, and m is 2 or 3.

19. The compound of claim 1 or 3 wherein m and n is each equal to 1, p is 0 to 1, and q is 0.

20. The compound of claim 19 wherein A^1 is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y^1 is –NH–.

21. The compound of claim 19 wherein A^1 is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y^1 is $-NH-SO_2-R^5-SO_2-NH-$, wherein R^5 is a divalent fluorinated group.

22. The compound of claim 19 wherein A^1 is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y^1 is $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$, wherein R^6 and R^7 are a divalent fluorinated groups.

23. A compound of claim 1 or 3 wherein the compound is a random copolymer obtained by randomly combining any variety of the polymer repeat units, in any ratio with respect to each other, wherein m and n are each equal to 1, p is 0 to 1 and q is 0.

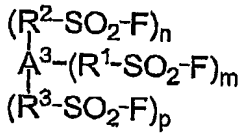
24. A compound of claim 1 or 2 wherein A^1 is a divalent aromatic heterocyclic group, m is 2, n and p are each equal to 0, and Y^1 is $-NH-SO_2-R^4$.

25. A compound of claim 1 or 3 wherein A^1 is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y^1 is –NH–.

26. A compound of claim 1 or 3 wherein A^1 is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y^1 is $-NH-SO_2-R^5-SO_2-NH-$.

27. A compound of claim 1 or 3 wherein A^1 is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y^1 is $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$.

28. A fluorinated fluorosulfonyl-substituted heterocycle having the general structure:



(II),

wherein A^3 is a divalent or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R^1, R^2, and R^3 are divalent fluorinated groups;

m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 2 or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by fluorinated fluorosulfonyl groups.

29. The fluorinated fluorosulfonyl-substituted heterocycle of claim 28 wherein A^3 is a divalent aromatic heterocyclic group, m and n are each equal to 1, and p is 0.

30. The fluorinated fluorosulfonyl-substituted heterocycle of claim 28 wherein A^3 is a divalent aromatic heterocyclic group, n and p are each equal to 0, and m is 2.

31. A process for synthesizing a compound comprising the following steps:

(a) providing a fluorosulfonyl-containing acyl derivative having the structure:

$$F\text{-}SO_2\text{-}R^8\text{-}X,$$

wherein R^8 is a divalent fluorinated group as defined above for R^1 and X is an acyl group;

(b) condensing the fluorosulfonyl-containing acyl derivative from step (a) with a nitrogenous reagent to form a sulfonyl-containing precursor;

(c) cyclizing the sulfonyl-containing precursor of step (b) by thermolysis or dehydration to form a sulfonyl-containing aromatic heterocyclic compound containing fluorosulfonyl groups or sulfonamide groups; and

(d) converting the sulfonyl-containing aromatic heterocyclic compound of step (c) containing fluorosulfonyl groups or sulfonamide groups, into an acidic sulfonyl-containing aromatic heterocyclic compound by either:

(i) condensing fluorosulfonyl groups with a fluorinated sulfonamide,

(ii) condensing sulfonamide groups with a fluorinated sulfonyl fluoride,

(iii) condensing fluorosulfonyl groups first with ammonia to form sulfonamide groups followed by a fluorinated sulfonyl fluoride to

form sulfonimide groups, or

(iv) hydrolysis of fluorosulfonyl or sulfonamide groups to form sulfonic acid groups.

32. The process of claim 31 wherein the acyl group is selected from the group consisting of acyl fluoride, acyl chloride, acyl bromide, acyl iodide, an ester, an amide, and nitrile.

33. The process of claim 31 wherein the nitrogenous reagent, is selected from the group consisting of ammonia; hydrazine; an azide; and an organic ortho-substituted aromatic amine.

34. A process for synthesizing a bis(sulfonimide)-[1,3,4]oxadiazole by condensing a fluorosulfonyl acyl fluoride, F-SO_2-R^6-CO-F, with hydrazine to form a bis(fluorosulfonyl)dihydrazide containing a dihydrazide group and fluorosulfonyl groups; forming a [1,3,4]oxadiazole ring by cyclizing the dihydrazide group using dehydration; condensing the fluorosulfonyl groups with ammonia to form a bis(sulfonamide)-[1,3,4]oxadiazole containing sulfonamide groups; and forming sulfonimide groups by condensing a fluorinated sulfonyl fluoride, R^4-SO_2-F, with the sulfonamide groups, wherein R^4 and R^8 are linear perfluorinated saturated groups having 1 to 6 carbon atoms.

35. A process for synthesizing a copolymer containing sulfonimide and [1,3,4]oxadiazole groups by condensing a fluorosulfonyl acyl fluoride, F-SO_2-R^6-CO-F, with hydrazine to form a bis(fluorosulfonyl)dihydrazide containing a dihydrazide group and fluorosulfonyl groups; forming a [1,3,4]oxadiazole ring by cyclizing the dihydrazide group using dehydration; condensing the fluorosulfonyl groups with ammonia to form a bis(sulfonamide)-[1,3,4]oxadiazole containing sulfonamide groups; and forming sulfonimide groups by condensing a fluorinated disulfonyl difluoride, F-SO_2-R^5-SO_2-F, with the sulfonamide groups, wherein R^5 and R^8 are linear perfluorinated saturated groups having 1 to 6 carbon atoms.

36. A process for synthesizing a benzimidazole sulfonimide by condensing a fluorosulfonyl acyl fluoride, F-SO_2-R^6-CO-F, with ammonia to form a diamide containing a carbamide group and a sulfonamide group; condensing the carbamide group with an ortho-phenylene diamine to form a carbamide adduct; cyclizing the carbamide adduct by thermolysis to form a benzimidazole group, and forming a sulfonimide group by condensing a fluorinated sulfonyl fluoride, R^4-SO_2-F, with the sulfonamide group,

wherein R^4 and R^8 are linear perfluorinated saturated groups having 1 to 6 carbon atoms.

37. A process for synthesizing a benzimidazole sulfonic acid by condensing a fluorosulfonyl acyl fluoride, $F\text{-}SO_2\text{-}R^8\text{-}CO\text{-}F$, with an ortho-phenylene diamine to form a carbamide adduct; cyclizing the carbamide adduct by thermolysis to form a benzimidazole group, and forming a sulfonic acid group by hydrolyzing the fluorosulfonyl group wherein R^8 is a linear perfluorinated saturated group having 1 to 6 carbon atoms.

38. A solid polymer electrolyte membrane comprising a porous substrate having imbibed therein a compound having the general structure:

$$\begin{array}{l}(R^2\text{-}SO_2\text{-}(Y^2)_q)_n \\ \quad\uparrow \\ A^1\text{-}(R^1\text{-}SO_2\text{-}Y^1)_m \\ \quad\uparrow \\ (R^3\text{-}SO_2\text{-}Y^3)_p\end{array} \qquad (I),$$

wherein A^1 is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R^1, R^2, and R^3 are divalent fluorinated groups;

m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups;

q is 0 or 1;

Y^1 is –OH, $\text{–NH-SO}_2\text{-}R^4$ wherein R^4 is a monovalent fluorinated group, –NH–, $\text{–NH-SO}_2\text{-}R^5\text{-SO}_2\text{-NH–}$, or $\text{–NH-SO}_2\text{-}R^6\text{-}A^2\text{-}R^7\text{-SO}_2\text{-NH–}$, wherein A^2 is a divalent aromatic heterocyclic group and R^5, R^6, and R^7 are divalent fluorinated groups; and

Y^2 and Y^3 are –OH or $\text{–NH-SO}_2\text{-}R^4$; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y^1 is selected from the group consisting of –NH–, $\text{–NH-SO}_2\text{-}R^5\text{-SO}_2\text{-NH–}$, and $\text{–NH-SO}_2\text{-}R^6\text{-}A^2\text{-}R^7\text{-SO}_2\text{-NH–}$.

39. The solid polymer electrolyte membrane of claim 38 wherein the porous substrate is selected from the group consisting of inorganic fiber substrates and microporous films of perfluorinated polymers.

40. The solid polymer electrolyte membrane of claim 38 wherein the compound is a small molecule.

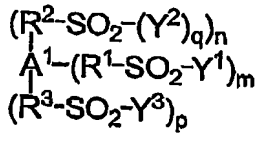
41. The solid polymer electrolyte membrane of claim 38 wherein the compound is a repeat unit for a polymer.

42. The solid polymer electrolyte membrane of claim 38 wherein the compound is cross linked, grafted, or chain extended within the porous support.

43. The solid polymer electrolyte membrane of claim 42 wherein the compound is modified to contain reactive functional groups to provide crosslinking, grafting, or chain extension.

44. The solid polymer electrolyte membrane of claim 42 wherein the compound is mixed with reagents to provide crosslinking, grafting, or chain extension.

45. A catalyst coated membrane comprising a solid polymer electrolyte membrane having a first surface and a second surface, an anode present on the first surface of the solid polymer electrolyte membrane, and a cathode present on the second surface of the solid polymer electrolyte membrane, wherein the solid polymer electrolyte membrane comprises a porous substrate having imbibed therein a compound having the general structure:



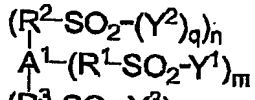
(I),

wherein A^1 is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R^1, R^2, and R^3 are divalent fluorinated groups;

m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups;
q is 0 or 1;
Y^1 is –OH, –NH-SO_2-R^4 wherein R^4 is a monovalent fluorinated group, –NH–, –NH-SO_2-R^5-SO_2-NH–, or –NH-SO_2-R^6-A^2-R^7-SO_2-NH–, wherein A^2 is a divalent aromatic heterocyclic group and R^5, R^6, and R^7 are divalent fluorinated groups; and
Y^2 and Y^3 are –OH or –NH-SO_2-R^4; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y^1 is selected from the group consisting of –NH–, –NH-SO_2-R^5-SO_2-NH–, and –NH-SO_2-R^6-A^2-R^7-SO_2-NH–.

46. A membrane electrode assembly comprising a polymer electrolyte membrane having a first surface and a second surface, and comprising a compound having the general structure:

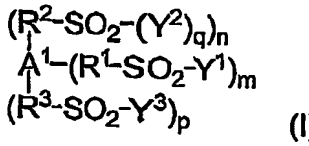


(I),

wherein A^1 is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;
R^1, R^2, and R^3 are divalent fluorinated groups;
m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups;
q is 0 or 1;
Y^1 is –OH, –NH-SO_2-R^4 wherein R^4 is a monovalent fluorinated group, –NH–, –NH-SO_2-R^5-SO_2-NH–, or –NH-SO_2-R^6-A^2-R^7-SO_2-NH–, wherein A^2 is a divalent aromatic heterocyclic group and R^5, R^6, and R^7 are divalent fluorinated groups; and

Y^2 and Y^3 are –OH or –NH-SO_2-R^4; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y^1 is selected from the group consisting of –NH–, –NH-SO_2-R^5-SO_2-NH–, and –NH-SO_2-R^6-A^2-R^7-SO_2-NH–.

47. An electrocatalyst coating composition comprising a compound having the general structure:



(I),

wherein A^1 is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R^1, R^2, and R^3 are divalent fluorinated groups;

m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups;

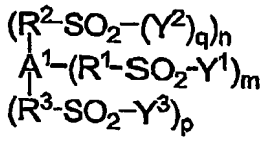
q is 0 or 1;

Y^1 is –OH, –NH-SO_2-R^4 wherein R^4 is a monovalent fluorinated group, –NH–, –NH-SO_2-R^5-SO_2-NH–, or –NH-SO_2-R^6-A^2-R^7-SO_2-NH–, wherein A^2 is a divalent aromatic heterocyclic group and R^5, R^6, and R^7 are divalent fluorinated groups; and

Y^2 and Y^3 are –OH or –NH-SO_2-R^4; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y^1 is selected from the group consisting of –NH–, –NH-SO_2-R^5-SO_2-NH–, and –NH-SO_2-R^6-A^2-R^7-SO_2-NH–.

48. An electrocatalyst coating composition of claim 47 further comprising a catalyst.

49. An electrochemical cell comprising a polymer electrolyte membrane, wherein the polymer electrolyte membrane comprises a compound having the general structure:



(I),

wherein A^1 is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R^1, R^2, and R^3 are divalent fluorinated groups;

m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups;

q is 0 or 1;

Y^1 is –OH, –NH-SO_2-R^4 wherein R^4 is a monovalent fluorinated group, –NH–, –NH-SO_2-R^5-SO_2-NH–, or –NH-SO_2-R^6-A^2-R^7-SO_2-NH–, wherein A^2 is a divalent aromatic heterocyclic group and R^5, R^6, and R^7 are divalent fluorinated groups; and

Y^2 and Y^3 are –OH or –NH-SO_2-R^4; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y^1 is selected from the group consisting of –NH–, –NH-SO_2-R^5-SO_2-NH–, and –NH-SO_2-R^6-A^2-R^7-SO_2-NH–.

50. The electrochemical cell of claim 49 selected from the group consisting of fuel cells, batteries, chloralkali cells, electrolysis cells, sensors, electrochemical capacitors, and modified electrodes.